

CLEAN PRODUCTION OF COKE

FIELD OF THE INVENTION

The present invention relates generally to clean production of coke and more particularly to the use of two types of carbon, one of which comprises low quality coal fines, such as waste coal fines, and/or waste coke or char fines which, after mixing, may be fired without formation into objects or formed into objects and fired to produce solid pyrolyzed objects or pieces, with by-products from pyrolyzation being recycled for use within the coke-producing closed system.

BACKGROUND

Coke heretofore has conventionally been produced from high quality sources of carbon, such as high quality coking coals. Prior processes and apparatus for conventionally producing coke typically are open or partly open systems, which generate by-products released to pollute the atmosphere.

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BRIEF SUMMARY AND OBJECTS OF THE PRESENT INVENTION

In brief summary, the present invention overcomes or substantially alleviates problems associated with prior ways of conventionally producing coke. The present invention may be summarized as comprising closed system apparatus and processes by which carbon feedstock, comprised of a mixture of non-coking coal and/or another carbonaceous material, such as waste coke fines, are mixed together and pyrolyzed into coke either as solid pieces or not. When solid pieces or objects of the mixture are formed, they are fired through pyrolyzation into solid pieces of coke, with solid and/or liquid and gaseous by-products of pyrolyzation being recycled for use within the closed coke-producing system, thereby eliminating release of undesirable substances to the atmosphere. Feedback tars, with or without a char-forming binder, is added to the carbon mixture prior to pyrolyzation.

With the foregoing in mind, it is a primary object of the present invention to overcome or substantially alleviate problems of the past associated with production of coke.

Another paramount object of the present invention is to produce a novel form of coke and to do so using novel apparatus and unique processes.

A further dominant object is to produce coke from a mixture comprising low quality or non-coking coal fines, which mixture is pyrolyzed into high quality coke.

Another important object is to produce coke from a mixture comprising waste coke fines, which mixture is pyrolyzed into high quality coke.

An additional object of importance is to produce coke so as to avoid contaminating the environment by recycling or recirculating solid and/or liquid and gaseous by-products within the closed coke-producing system.

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These and other objects and features of the present invention will be apparent from the detailed description taken with reference to the accompanying drawings.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a flow diagram of one process by which low quality coal and another carbonaceous material, such as waste coke fines, are transformed into metallurgical and other grades of coke; and

Figure 2 is a flow diagram of another similar process by which low quality coal and other carbonaceous material is transformed into metallurgical and other grades of coke.

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DETAILED DESCRIPTION

Waste carbonaceous fines have not heretofore been used in the commercial production of coke. Coke is a fuel universally used in the iron and steel industry. Currently, nearly all metallurgical and foundry coke is produced in conventional coke oven facilities requiring the use of good quality coking coals. These coals are becoming scarce, difficult to mine, and, therefore, expensive. Because of the high costs, decreasing supply of these feedstock materials, and environmental contamination problems associated with current coke-making practices, there is a need for alternative coke-making and coke supplementing technologies. Prior attempts to use various form coke processes have primarily resulted in commercial failure and, furthermore, excess by-products of pyrolysis are generated in such processes, which must be refined into salable liquid fuels. Elimination of the need to process and market excess aromatic tars from form coke processes has been a problem. The present invention addresses these problems and provides processes by which waste coke fines (including coke breeze generated from conventional coking processes or petroleum coke) with coal fines are blended to produce a high quality coke product.

These coke processes do not require high quality coking coals nor are a surplus of pyrolytic products produced. Non-coking coal fines and coke fines may be blended together in such proportions that production of pyrolysis by-products is limited to the amount required for binding and for process heat. Feedback tar may be combined with additional synthetic or natural binder to produce prime quality solid coke pieces or objects, such as briquettes or blocks. The process 1) uses feedstock material more efficiently than other form coke processes by eliminating discharge of secondary, low value by-products, and 2) uses undesirable materials and industrial wastes not

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FOI b7D b7C b7E b7F b7G b7H b7I b7J b7K b7L b7M b7N b7O b7P b7Q b7R b7S b7T b7U b7V b7W b7X b7Y b7Z b7AA b7AB b7AC b7AD b7AE b7AF b7AG b7AH b7AI b7AJ b7AK b7AL b7AM b7AN b7AO b7AP b7AQ b7AR b7AS b7AT b7AU b7AV b7AW b7AX b7AY b7AZ b7BA b7BB b7BC b7BD b7BE b7BF b7BG b7BH b7BI b7BJ b7BK b7BL b7BM b7BN b7BO b7BP b7BQ b7BR b7BS b7BT b7BU b7BV b7BW b7BX b7BY b7BZ b7CA b7CB b7CC b7CD b7CE b7CF b7CG b7CH b7CI b7CJ b7CK b7CL b7CM b7CN b7CO b7CP b7CQ b7CR b7CS b7CT b7CU b7CV b7CW b7CX b7CY b7CZ b7DA b7DB b7DC b7DD b7DE b7DF b7DG b7DH b7DI b7DJ b7DK b7DL b7DM b7DN b7DO b7DP b7DQ b7DR b7DS b7DT b7DU b7DV b7DW b7DX b7DY b7DZ b7EA b7EB b7EC b7ED b7EE b7EF b7EG b7EH b7EI b7EJ b7EK b7EL b7EM b7EN b7EO b7EP b7EQ b7ER b7ES b7ET b7EU b7EV b7EW b7EX b7EY b7EZ b7FA b7FB b7FC b7FD b7FE b7FF b7FG b7FH b7FI b7FJ b7FK b7FL b7FM b7FN b7FO b7FP b7FQ b7FR b7FS b7FT b7FU b7FV b7FW b7FX b7FY b7FZ b7GA b7GB b7GC b7GD b7GE b7GF b7GG b7GH b7GI b7GJ b7GK b7GL b7GM b7GN b7GO b7GP b7GQ b7GR b7GS b7GT b7GU b7GV b7GW b7GX 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b7EE b7EF b7EG b7EH b7EI b7EJ b7EK b7EL b7EM b7EN b7EO b7EP b7EQ b7ER b7ES b7ET b7EU b7EV b7EW b7EX b7EY b7EZ b7FA b7FB b7FC b7FD b7FE b7FF b7FG b7FH b7FI b7FJ b7FK b7FL b7FM b7FN b7FO b7FP b7FQ b7FR b7FS b7FT b7FU b7FV b7FW b7FX b7FY b7FZ b7GA b7GB b7GC b7GD b7GE b7GF b7GG b7GH b7GI b7GJ b7GK b7GL b7GM b7GN b7GO b7GP b7GQ b7GR b7GS b7GT b7GU b7GV b7GW b7GX b7GY b7GZ b7HA b7HB b7HC b7HD b7HE b7HF b7HG b7HH b7HI b7HJ b7HK b7HL b7HM b7HN b7HO b7HP b7HQ b7HR b7HS b7HT b7HU b7HV b7HW b7HX b7HY b7HZ b7IA b7IB b7IC b7ID b7IE b7IF b7IG b7IH b7II b7IJ b7IK b7IL b7IM b7IN b7IO b7IP b7IQ b7IR b7IS b7IT b7IU b7IV b7IW b7IX b7IY b7IZ b7JA b7JB b7JC b7JD b7JE b7JF b7JG b7JH b7JI b7JJ b7JK b7JL b7JM b7JN b7JO b7JP b7JQ b7JR b7JS b7JT b7JU b7JV b7JW b7JX b7JY b7JZ b7KA b7KB b7KC b7KD b7KE b7KF b7KG b7KH b7KI b7KJ b7KK b7KL b7KM b7KN b7KO b7KP b7KQ b7KR b7KS b7KT b7KU b7KV b7KW b7KX b7KY b7KZ b7LA b7LB b7LC b7LD b7LE b7LF b7LG b7LH b7LI b7LJ b7LK b7LM b7LN b7LO b7LP b7LQ b7LR b7LS b7LT b7LU b7LV b7LW b7LX b7LY b7LZ b7MA b7MB b7MC b7MD b7ME b7MF b7MG b7MH b7MI b7MJ b7MK b7ML b7MN b7MO b7MP b7MQ b7MR b7MS b7MT b7MU b7MV b7MW b7MX b7MY b7MZ b7NA b7NB b7NC b7ND b7NE b7NF b7NG b7NH b7NI b7NJ b7NK b7NL b7NM b7NO b7NP b7NQ b7NR b7NS b7NT b7NU b7NV b7NW b7NX b7NY b7NZ b7OA b7OB b7OC b7OD b7OE b7OF b7OG b7OH b7OI b7OJ b7OK b7OL b7OM b7ON b7OO b7OP b7OQ b7OR b7OS b7OT b7OU b7OV b7OW b7OX b7OY b7OZ b7PA b7PB b7PC b7PD b7PE b7PF b7PG b7PH b7PI b7PJ b7PK b7PL b7PM b7PN b7PO b7PP b7PQ b7PR b7PS b7PT b7PU b7PV b7PW b7PX b7PY b7PZ b7QA b7QB b7QC b7QD b7QE b7QF b7QG b7QH b7QI b7QJ b7QK b7QL b7QM b7QN b7QO b7QP b7QQ b7QR b7QS b7QT b7QU b7QV b7QW b7QX b7QY b7QZ b7RA b7RB b7RC b7RD b7RE b7RF b7RG b7RH b7RI b7RJ b7RK b7RL b7RM b7RN b7RO b7RP b7RQ b7RR b7RS b7RT b7RU b7RV b7RW b7RX b7RY b7RZ b7SA b7SB b7SC b7SD b7SE b7SF b7SG b7SH b7SI b7SJ b7SK b7SL b7SM b7SN b7SO b7SP b7SQ b7SR b7SS b7ST b7SU b7SV b7SW b7SX b7SY b7SZ b7TA b7TB b7TC b7TD b7TE b7TF b7TG b7TH b7TI b7TJ b7TK b7TL b7TM b7TN b7TO b7TP b7TQ 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heretofore used to produce coke (i.e., low quality coal and/or coke or char fines) as a feedstock which represent a current serious environmental problem.

Energy savings for a steel plant can be exemplified by assuming a typical coke fines waste rate of 10% of the total coke production. Energy savings are noted in the increased utilization of raw materials, including extraction, transportation, and differences in processing requirements. Based on a steel mill capacity of about 6,000 tons of hot metal (THM)/day this represents an energy savings of about 4.5×10^{11} kJ/year over current technology.

Capital costs for the briquetting or solid objects portion of the process have been estimated based on other similar briquetting operations at between \$20-30 million for a one-half million ton/year plant. Raw material costs are estimated to be in the range of \$10/ton for waste coal fines and \$20/ton for coke fines. The processing costs for briquetting or formation of solid objects, which include the price of the additional natural or synthetic binder, if used, are estimated to be around \$18/ton, depending on the type of binder. Total costs for coke production from the process are expected to be in the range of \$50-60/ton. Current metallurgical coke prices are in the range of \$100-120/ton and foundry coke is \$140-160/ton. For a steel plant producing 6,000 THM/day, at an approximate rate of 500 lbs coke/THM, by incorporating the proposed process, a net savings of \$3.3 to \$2.8 million/year is expected.

The ability to utilize this new coke product, as a partial coke replacement in the blast furnace, will ultimately be proven by such an application. The properties of coke produced using the present invention compare well with other cokes previously or currently used as blast furnace fuels.

One concern regarding the use of form coke, made from a previous process, in a blast furnace is that its reactivity tended to be higher than standard metallurgical coke produced in slot ovens. The

new coke produced according to the present invention is expected to be able to replace oven-coke and have reactivities and strengths as good as or better than standard metallurgical coke.

As stated above, coke is a universal fuel used in the iron and steel industry. Metallurgical coke is commonly required for operation of iron ore reduction facilities, such as blast furnaces. Foundry coke is required for scrap melting in cupolas and in casting operations. Coke is also an important fuel for other applications, such as the phosphate industry.

The American steel industry underwent a major restructuring during the 1980's, resulting in the closing of many steel and coke-making plants. From 1980 to 1990, approximately 40% of the United States coke-making capacity was shut down. During this same time, very few new coke-making facilities were built. Today, approximately 26 million tons of metallurgical coke and 2 million tons of foundry coke are produced annually in the United States. Many of the remaining coking facilities are approaching the end of, or have been extended beyond, their life expectancies. Nearly 50% of the current capacity is over 20 years old and 40% is over 30 years old. These older facilities are not only expensive to maintain and operate but they are difficult to keep in compliance with environmental regulations.

Nearly all metallurgical and foundry coke is produced in conventional coke oven facilities requiring the use of high quality coking coals. Prime coking coals tend to have a volatile content between 19-33%. These coals are becoming scarce, difficult to mine, and, therefore, expensive. In 1995, the average delivered price for metallurgical coking coals in the U.S. was over \$47/ton while steam coals were about \$27/ton.

Coke ovens have for some time been of serious environmental concern due to the release of particulate and sulfur gases, as well as emissions of carcinogenic and mutagenic polycyclic aromatic

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hydrocarbons (PAHs) and benzene-toluene-xylenes (BTX). Consequently, the coke-manufacturing industry is being subjected to increasingly stringent environmental regulations. Advances in coke oven design, such as non-recovery ovens and jumbo coking reactors, show some environmental advantages but still require expensive coking coals to operate and represent a very large capital investment. As environmental regulations become more stringent, existing coking facilities will continue to be closed and capacity reduced. Furthermore, the high capital cost of building new cokemaking plants based on current technology and dwindling supplies of domestic prime coking coals has caused U.S. companies to look outside the country for coke supplies. The United States already imports a sizable quantity of coke, some produced from its own exported metallurgical coals. Because of the high costs, decreasing supply of feedstock materials, and environmental problems associated with current coke-making and coke supplementing technologies.

An alternative to producing coke from metallurgical coals in conventional slot ovens, is to use various form coke processes. Form coke is a term which generally describes carbonized, briquetted or otherwise formed fuel, made from pyrolyzed coal chars. In a process known as the FMC process, the coal is crushed and then charred at temperatures between 600 and 800°C, then mixed with a binder, briquetted, and finally carbonized at 900-1000°C. The initial partial devolatilization is designed to prevent swelling or sticking of the briquettes during the high temperature treatment. The binders needed for this briquetting are usually obtained from the combined by-products and tars generated during the low and high temperature charring and carbonizing steps. Most form coke processes can utilize non-coking coals for a portion of the feedstock, combined with expensive coking coals.

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Numerous form coke processes have been unsatisfactorily experimentally tested. Only a few have reached commercial production. Exceptions are the above-mentioned FMC Process, which converts sub-bituminous coal into pillow-shaped coke briquettes for phosphate production and, also, a process known as the CTC Process, which was commercially discontinued recently.

The FMC process requires multiple, staged, fluid-bed heaters to char and carbonize the coal. The tars are captured and used as a binder to form the char into briquettes which are calcined in a shaft furnace. The process incurs high capital costs.

The now discontinued CTC process used gasification to char the feed coal. The char was then crushed, hot-briquetted and finally calcined. By-products had to be refined into salable liquid fuels in order for the CTC process to be economically feasible. The CTC process utilized high grade coking coals for a portion of its feedstock.

By contrast, the present processes pertain to making briquettes from waste coke fines rather than coal char. A supplemental binder system, if used, may include combining a natural or synthetic binder with a carbonaceous binder such as tar, including but not limited to feedback tar from within the system. Extensive development and testing of the waste coke fines briquettes has been performed. Indications are that waste coke fines briquettes formed using the present invention, compare favorably with other successful form cokes, such as those obtained from the FMC and CTC processes. See TABLE 1, below:

TABLE 1

Comparison of briquettes from proposed process with other successful form cokes.				
Form Coke Type	Apparent Specific gravity	Abrasion Resistance	CSR	CRI
FMC ¹	0.8	69	47	75
CTC ²	1.2	54	30	15
New Process ³	1.4	80	50-70	15-30

1. Measured from samples obtained from FMC.

2. Data taken from Young and Musich, 1995.

3. Typical values measured from briquettes made using the present invention.

The economics of the present coke fines process is improved by: (1) use of feedback tar, resulting in the elimination of the need to import the tar portion of the binder and/or (2) elimination of the requirement to process and sell excess low-value tars. In order to do this, the present invention contemplates blending coke fines (e.g. coke breeze generated from conventional coking processes or petroleum coke) with waste non-coking coal fines. The coke breeze and/or petroleum coke fines and low grade coal fines are blended with a binder. The blend may be fed directly into the pyrolyzer or pressed into briquettes or other solid forms and subsequently cured. The relative mixture of coke fines with coal fines can be varied depending on the devolatilization products of the coal to obtain a process with closed material-loops where all of the products of devolatilization are used within the process.

During the pyrolysis operation, the temperature of the formed feedstock is elevated at a rate approximately within the range of 1500-2000°C/hr to a maximum temperature within the range of 800-1100°C. The devolatilization behavior of the feedstock varies during heat-up, depending on the feedstock mixture, but gases and tar evolve, leaving a carbon matrix behind.

Devolatilization behavior depends on many factors such as peak temperature, heating rate, particle size and coal type. General trends are that occluded carbon dioxide and methane are driven off at about 200°C. Above this temperature, internal condensation occurs among the macromolecular structures with the evolution of carbon dioxide and water.

In the range of 200-500°C, methane begins to evolve with its higher homologues and olefin. Most of the oxygen in coal structures is eliminated as water and oxides of carbon. The decomposition of both nitrogen structures and organic sulfur species begins in this temperature range.

The evolution of hydrogen begins at 400-500°C with a critical point at about 700°C characterized by a rapid evolution of hydrogen and carbon monoxide.

In the temperature range of 500-700°C, the volume of gases such as hydrogen, carbon monoxide, methane, and nitrogen increase with increasing temperature, while most hydrocarbons decrease.

Tar formation begins at around 300-400°C, with a maximum yield occurring at approximately 500-550°C, depending on heating rate and particle size. The character and composition of the tars will vary with temperature. Low-temperature tar usually consists mainly of olefin, paraffin hydrocarbons, and cyclic hydroaromatic structures. The aromatic nature of tar increases with increasing temperature until high-temperature tars are composed mostly of aromatic hydrocarbons.

The tars which evolve from the coal fines are captured and returned to be used as a binder. Fuel rich gases are used to operate the pyrolysis furnace. The idea of recycling tar to be used as the binder is not unique, standing alone. Many form coke processes utilize this step, among many others. However, since prior form coke processes typically use only raw coal in their feedstock they

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TABLE 2

Approximate product yields at 900°C of constituents in mix (ash free basis)			
Constituent	Fixed Carbon	Tars	Gases
Coke	100	0	0
Bituminous Coal	52	30	18
Tar Binder	40	40	20

If these components are blended in the mixture fractions given above, then the resulting products are 77% fixed carbon (coke product), 15% tars (used as a binder on a recycle basis), and 8% gas (used to fuel the pyrolyzer). This gas consists of about 25% water and carbon dioxide, leaving about 6% of the total feed as a combustible gas. The heating value of this gas is typical of coke oven gas (about 21,600 kJ/kg). About 1300 kJ of energy in the form of fuel rich gas is produced per kilogram of uncoked briquettes. The amount of energy required to raise the temperature of the briquettes from ambient to 900°C is 1100 kJ/kg, assuming a specific heat of coal of 1.26 kJ/kg°K. Therefore, to produce the proper amount of tars required within the process, the attending amount of evolved combustible gas is sufficient to operate a pyrolysis unit at 84% thermal efficiency. The feedstock mix can be adjusted according to pyrolysis product requirements. During the pyrolysis step, the original briquettes typically will lose only about 20-25% of their weight as opposed to 35-50% in prior form coke processes. Thus, briquettes or other solid objects obtained from the present invention have a higher product yield.

In summary, among other advantages, the proposed process: 1) utilizes low-value carbon fines to produce a high-value coke product; and 2) operates with closed material loops so that the sale of low-value, secondary products is not required to enhance its economic viability, a characteristic of prior form coke processes.

TO 2760-01015660

Nearly all metallurgical and foundry coke is produced in conventional, by-product recovery, horizontal slot ovens, requiring high quality coking coals as a raw material. The evolutionary development of conventional coke ovens is approaching its technological and economic limits. Because of this, several alternative coking processes have been attempted. Some of these are variations of the slot-oven type of systems including the Jewell-Thompson non-recovery coke oven and the Jumbo coking reactor. The goal of these types of slot oven technologies is to improve the efficiency and environmental friendliness in the production of coke. However, the economics of producing coke using these new technologies is not an improvement over conventional coke ovens. Another disadvantage of the new slot oven technologies is that they still require prime coking coals as a feedstock, which coking coals are becoming scarce, difficult to mine, and, therefore, expensive.

One type of emerging coking technology, different from the slot oven approach are form coke processes, discussed briefly above. A wide range of coals have been tested and some of the processes have produced form coke, the strength and reactivity of which are in an acceptable range for blast furnace use. However, strength tends to be at the low end and reactivity at the high end of that which is generally acceptable. These processes are performed in closed systems, making them very environmentally attractive. Their commercialization has been impeded due to economic considerations and product quality.

A typical form coking practice requires that the process be divided into three steps; 1) coal pyrolysis to form a dense char, 2) briquetting of the char with a binder, and 3) curing the resulting briquettes. Simply binding coal fines together and curing the resulting briquettes is not acceptable. The resulting briquettes exhibit considerable mass loss (35-50%), are small, laden with stress cracks, structurally weak, and likely too reactive. Excess by-products, such as coal tars, must be collected

and sold to make the process economically feasible. Due to the high cost of processing these by-products and their aromatic nature they must often be sold as low quality feedstock materials to refiners at a low price.

The processes of the present invention allow the coal pyrolysis and briquette curing processes to be combined. It does not require coking coals nor does it necessarily produce a surplus of pyrolytic products. Coal fines and coke fines are blended together in such proportions that just the amount of pyrolysis products are produced needed for perpetuating the binding and heating phases. The tar portion of the binder may be supplemented with a synthetic or natural binder, as appropriately determined by those skilled in the art, which produces a prime quality coke briquette or block. Since dense, low reactivity discarded or waste coke fines from conventional coke ovens or petroleum refining operations are used as a portion of the feedstock, product mass loss is significantly reduced, resulting in a strong product, where reactivity is lowered.

While the present processes more efficiently use feedstock material than is true of the prior form coke processes, there is another very significant feature of the present processes. The feedstock used within this process (i.e. coke fines and coal fines) are normally discarded and classified as either wastes or undesirable materials, representing a current environmental problem. Coke breeze produced at existing coking plants cannot per se be utilized within the blast furnace and must either be disposed of, or sold at a relatively low cost. Delayed petroleum coke fines and fluid-coke are often landfilled. Coal fines are currently either disposed of in slurry ponds or are landfilled. The transformation of these waste materials into a high value coke is a surprising and valuable step forward.

TO 160-1091560

Tremendous energy resources are normally associated with coal and coke-intensive industries such as mining, iron and steel production, metal castings, and other manufacturing processes. During normal materials handling, significant amounts of fines are generated which, in the best case, can be sold as a low quality product, but typically are landfilled. This loss of raw material is about 5-15% of the total coal or coke production and represents a significant energy loss. The present processes allow the steel and mining industries to minimize disposal by utilizing heretofore unused, potentially valuable wastes, thus reducing material costs, land-fill charges and other expenses. Energy savings occur as the consumption of raw materials and the generation of land-filled waste is reduced. This innovative technology significantly reduces wastes generated from coking and mining operations and represents a high end use for petroleum coke fines. Like all effective process-specific recycles, the amount of raw materials input for a given output is reduced.

Energy savings are noted in the increased utilization of raw materials, including extraction, transportation, and differences in processing requirements. Energy savings for a steel plant producing 6,000 THM per day can be exemplified by reasonably assuming a typical coke fines generation rate of 10% of the total coke production. Use of the briquettes represents a more than 1 to 1 savings in raw materials, since the briquette replaces both the raw material of appropriate size and the feedstocks that would have been discarded since they were too fine. To produce the additional coke required to compensate for the generation of fines that are too small to use, for the plant size described, requires approximately 1.1×10^{12} kJ/year. To convert those fines into a useable coke product using the proposed process requires only about 6.5×10^{11} kJ/year. The resulting energy savings is about 4.5×10^{11} kJ/year. Other similar values could be obtained for the chemical processing, castings, and other coke consuming industries.

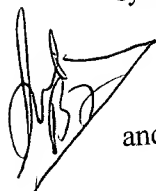
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The capital cost of installing a coke works at an iron production facility represents a significant portion (about 40%) of the overall required capital cost. In 1987 the annual investment costs per ton of coke production was \$46-\$65. The 1987 maintenance and repair costs were estimated at about \$2.50-\$3.25/ton. The growing emphasis on safeguarding the environment, both the working environment for the operators and the general environment outside the works boundary, is escalating the cost of coke ovens. The cost of the new 2 million ton/year Kaiserstuhl III coke works was about \$800 million, including the cost for coke quenching and the by-products plant. The rebuilding of a 900,000 ton/year plant at the Great Lakes Division of National Steel cost in excess of \$450 million. It has been argued that the Kaiserstuhl III works represents the highest development potential of slot-type coke ovens and that a radical departure from the classical design is needed to achieve any major reduction in the cost of coke production.

The cost associated with form coke plants can vary according to the process requirements. Capital costs for the 1 million ton/year FMC plant was estimated at \$350 million in 1992. Operating costs were very sensitive to raw material costs and were most favorable for western coals priced at \$10/ton, where 60% of the coal weight is lost in the process, as by-products. Total costs associated with coke production were stated to be about \$63/ton using western coals, \$90/ton with midwestern coals, and \$107/ton with eastern coking coals. The costs for western and midwestern coals assume a credit for sale of by-products.

Detailed capital and operating costs associated with the present processes remains to be precisely determined. However, some comparisons with other processes can be made. Capital costs for the present briquetting operations have been estimated, based on other similar briquetting operations, at between \$20-30 million for a one-half million ton/year plant. Estimates of operating

costs for a briquetting plant of this size include raw materials costs and processing costs. Raw materials costs are estimated to be in the range of \$10/ton for waste coal fines and \$20/ton for coke fines. The processing costs for briquetting, which include the price of an additional natural or synthetic binder, are estimated to be around \$18/ton, depending on the type of binder.

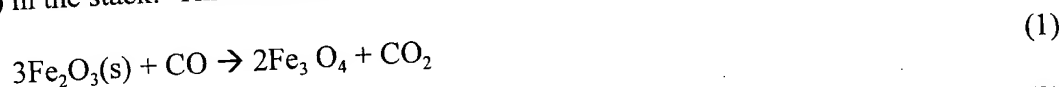
 An FMC formed coke plant, as stated above, uses multiple fluidized beds for char production and a curing oven and calciner for coke production. The processing and capital costs associated with commercial use of the present technology are expected to be much lower than for prior form coke processes, since the char production step is eliminated. Total costs for coke production from the present process are likely to be in the range of \$50-60/ton, without requiring the sale of by-products. Current metallurgical coke prices are in the range of \$100-120/ton and foundry coke is \$140-160/ton.

For a steel plant producing 6,000 THM/day, at an approximate rate of 500 lbs coke/THM and at an approximate cost of \$100/ton for coke, the replacement value of the coke normally lost would be about \$5.5 million a year. Reduction in the amount purchased, since all the coke is initially used or reclaimed and used, represents another 1% or \$0.55 million. With briquette costs expected to be around \$50-60/ton, a net savings of \$3.3 to \$2.8 million/year is expected.

The characteristics of supplemental coke products and cokes made from alternative coking technologies must fall within the strict standards necessary for its intended use. The most stringent requirements for coke are associated with blast furnace use. Metallurgical coke used in blast furnaces must be (1) a fuel to provide heat to meet the endothermic requirements of chemical reactions and melting of the slag and metal, (2) a producer and regenerator of reducing gases for the reduction of iron oxides, and (3) an agent to provide permeability for gas flow and support for furnace burden. Because of the many requirements placed on metallurgical coke, it must meet

stringent standards of strength, size and composition. As a fuel and producer of reducing gases, the carbon content should be maximized. As a regenerator of reducing gas, it should have an adequate reactivity to carbon dioxide and water vapor. To provide permeability and burden support, it should be charged in a narrow size range and experience minimal breakdown as it progresses through the blast furnace.

Different iron ore reduction reactions occur within the blast furnace, depending on furnace operation and temperature region. Indirect reduction occurs at relatively low temperatures (850-900°C) in the stack. This exothermic reaction can occur with carbon monoxide as follows:



and



The 'solution loss' reaction produces carbon monoxide from carbon dioxide reacting with coke above 900°C. It is highly endothermic or energy consuming.



At high temperatures in the lower part of the furnace, iron and carbon monoxide are produced by carbon reacting endothermically with iron oxide by the direct reduction reaction.



Decreasing direct reduction in favor of indirect reduction is advantageous because the latter is exothermic and lowers the overall heat requirements for the blast furnace. Increasing the CO or H₂ content of the blast furnace gas increases the rate of indirect reduction.

Standard testing procedures for cokes to qualify them for use in blast furnaces have been developed over the years, as the science and art of blast furnace operation and the requirements of coke have become better understood. Prior to 1993, standard coke tests included proximate analysis to determine chemical make-up, drop shatter and tumbler tests to determine strength, and specific gravity and porosity tests to measure structural characteristics. None of these tests were performed under conditions that the coke might encounter in the blast furnace, such as a harsh chemical environment, high pressure, and high temperature. In recent years, the Japanese steel industry developed a procedure that tests coke strength and breakdown to CO₂ attack under blast furnace conditions. In 1993, this test was adopted as an ASTM standard test for coke as ASTM D 5341-93 entitled Standard Test Method for Measuring Coke Reactivity Index (CRI) and Coke Strength After Reaction (CSR).

The joint CSR/CRI test heats a bed of coke in a nitrogen atmosphere to 1100°C in 30 minutes, reacts the coke sample in a flow of CO₂ for 120 minutes with the bed temperature constant at 1100°C, cools the sample to 100°C, transfers the sample to a tumbler, and tumbles the sample for 600 revolutions in 30 minutes. The sample is then sieved in a 3/8 inch sieve. The CSR is calculated as the remaining portion in the sieve compared to the amount removed from the furnace.

The purpose of the CRI test is to give insight into the ability of CO₂ to react with the carbon in the coke, a necessary reaction in the blast furnace but which must be controlled to prevent carbon from being consumed prematurely. The CSR test provides information about two different issues; 1) the strength of the briquettes after reacting with CO₂, and 2) the amount of dust produced by CO₂ attack and bed agitation. Fine dust can be detrimental in the blast furnace since it can decrease the permeability of the bed requiring increased blast pressure to force the air up through the bed.

Both the FMC and CTC Processes described above have demonstrated that they are able to produce form coke capable of blast furnace use. The FMC process utilizes subbituminous coals and lignites, and yields small ($1\frac{1}{4} \times 1\frac{1}{8} \times \frac{3}{4}$ in, or $\frac{7}{8} \times \frac{3}{4} \times \frac{1}{2}$ in) coke briquettes, that have performed well in experimental blast furnace trials. A comparison of FMC formed coke and a standard metallurgical coke is shown in TABLE 3 (Berkowitz, 1979) and some data from tests of FMC coke in a US Steel Corporation experimental blast furnace are summarized in TABLE 4 (Berkowitz, 1979).

TABLE 3

FMC Formed Coke Properties		
	FMC Coke	"Standard" Metallurgical Coke
Relative crushing strength, lb/in ²	3000	400-2000
(ASTM) Apparent density, gm/cm ³	0.8-1.2	0.85-1.3
Bulk density, lb/ft ³	30-45	20-30
Hardness, moh scale	6+	6+
Surface area, m ² /gm	50-200	1-25
Chemical reactivity, %/hr	15-50	1-5
Volatile matter, %	<3	1-2

TABLE 4

Experimental Blast-furnace Test Data		
	FMC Coke	"Standard" 2 x $\frac{3}{4}$ -in Metallurgical Coke
Sinter/coke, lb/lb	2.96	2.82
Coke rate, lb/ton hot metal	1062	1096
Production rate, lb/hr	3601	3384
Slag volume, lb/ton hot metal	604	600
Stack dust, lb/hr	20.2	12.7

The ability to utilize the present new coke product can be determined by comparing its properties with cokes that have been proven to be effective blast furnace fuels. TABLE 5 compares some of the advantages of coke fines briquettes produced according to the present invention with other cokes previously or currently used as blast furnace fuels and also lists what is accepted as a standard metallurgical coke (Berkowitz, 1979). While the coke fines / coal fines briquettes may vary somewhat from those produced with coke fines only, the properties will be similar. Testing of briquettes made with coal/coke blends show crush strength values of around 1400 psi.

TABLE 5

	Coke Properties		
	FMC Coke	Coke fines Briquettes	"Standard" Metallurgical Coke
Relative crushing strength, lb/in ²	600	1400-4000	400-2000
Apparent density, gm/cm ³	0.8-1.2	1.2-1.5	0.85-1.3
Bulk density, lb/ft ³	30-45	na	20-30
Surface area, m ² /gm	50-200	na	1-25
Relative CO ₂ reactivity (CRI)	60-75	15-30	20-30
Coke Strength (CSR)	40-50	50-75	50-65

Coals charged to standard coke ovens comprise a blend of coals with differing properties. Typically 3-5 coals are blended together in such proportions that the properties of the blend will produce a high quality coke product. If a weakly coking coal of low fusibility is used in the blend then the strongly coking coal component must be more fusible and higher in volatile matter to compensate. Therefore, even though mildly and weakly coking coals may be used in a particular blend, the blend would be formulated such that its properties would reflect the parameters outlined

below in TABLE 6. TABLE 6 lists referenced characteristics for high quality coking coals or blends (Van Krevelen, 1993.) Coal blends not meeting these characteristics would produce inferior coke.

As used in this specification, low quality coking coals are any coals, individually and collectively, that fall appreciably outside one or more of the parameters listed in TABLE 6. Although such coals may be included in a blend for standard coke oven use, they do not meet the requirements by themselves. Such coal or coals could be used as the sole source of coal within the new process.

TABLE 6

Main parameters to Characterize coals for carbonization (coking)

Parameter group	Parameters	Indicative values
Rank parameters	C-content, daf (%) H-content, daf (%) R_m (V-reflectance) VM-content, daf (%) CV (MJ/kg), mmmf	86-90 5.0 to 5.5 1.0 to 1.35 24-28 34-36
Rheological parameters (on heating)	FSI Dilation behavior Maximum fluidity	6.5-8 eu-plastic (ortho-pl. type) dil. 100 to 125% 900-1100
Parameters for Contaminants	Ash S	Less than 7 Less than 0.6

With reference to the drawings, in light of the foregoing presentation, numerals are used throughout to identify common parts. Figures 1 and 2 are flow diagrams of processes by which fine or particulate carbonaceous material, normally considered waste, is transformed into metallurgical and other grades of coke. Figures 1 and 2 are identical flow diagrams, except that char-forming binder is not added to the mix in the mixer 16. Accordingly, with this exception, the following description of Figure 1 applies also to Figure 2.

Two sources of feedstock are provided, i.e. low grade coal 10 and discarded or waste coke 12. Any suitable carbonaceous material, such as petroleum coke fines, coke breeze char, or carbon black, may comprise material 12, while, coal, or waste coal fines may comprise material 10. If unsatisfactorily large in size, the materials 10 and 12 can be crushed to a fine particle size. Material 10 and material 12, if not sufficiently particulate, are, therefore, crushed by a commercially available crusher 14, to obtain suitably sized fine particles. Any suitable crusher may be used provided, however, in most applications, the crusher must be able to reduce oversized material to about 1/4" or 1/8" and below. The percentages of the various materials being fed to the crusher 14 depend largely on the type of materials being fed. Typically, coal, petroleum coke, and in some cases, metallurgical coke breeze may be fed to the crusher. Coal may account for 20-40% of the mix, petroleum coke may be 40-70%, and metallurgical coke breeze 5-10% of the total mix.

The mixer 16 must be able to adequately combine the carbon fines and the feedback tars and pitches as well as integrate liquid synthetic and/or natural binders, if used. The fines comprising materials 10 and 12, crushed or not crushed as the case may be, are blended in mixer 16 with feedback tars including pitches, obtained during the process (Figure 2) or feedback tars obtained during the process are mixed with a suitable natural and/or synthetic binder (Figure 1). Suitable char-forming binders comprises tars, pitches, CAT bottoms and thermosetting resins.

Mixing continues until a desired homogeneous blend of the influent materials is obtained.

The effluent from the mixer 16 may be displaced into a solid object former 18, which may be a briquette machine when solid coke objects or pieces are desired. The former 18 compresses the mixture into a desired shape e.g. briquettes, blocks, etc. Formation of solid objects or pieces, such as briquettes, is optional, since coke is usable in a variety of forms. The mixture can be discharged

from the mixer 16 straight into the pyrolyzer 20, without formation into solid objects. Any suitable type of former may be used depending on the size and shape desired for the final product, as specified by the end user.

The solid objects, such as briquettes, from the former 18 are or material from the mixer 16 is introduced into a pyrolyzer 20, where the same is coked and prepared for final use. The pyrolyzer furnace 20 must be able to heat the feedstock to around 800-1100°C at a rate of 1500-2000°C/hr and be able to capture the resulting off-gases and tars. The Pyrolyzer 20 normally lowers the coke volatility below 2%. This typically requires temperatures of greater than 800°C, usually within the range of 800-1100°C. Heat-up rate is important to prevent cracking of final product and should be no greater than about 1500°C per hour. Coke, as solid objects or otherwise, is discharged from the pyrolyzer 20 at site 22.

During the pyrolyzing process, gases and tars evolve as by-products in the pyrolyzer 20. As they evolve they exit the pyrolyzer at site 24 and become the influent to a separator 28 at site 26. The separator 28 separates the by-product tars from the gases. The tars are discharged at site 30 and fed back as a binder into the mixer 16 at site 34, either with or without the addition of an additional char-forming synthetic and/or natural binder. The gases are discharged at site 32 and fed back as fuel for the pyrolyzer 20. The separator 28 must be able to collect the off-gases and cool, condense and collect the condensed tars.

The exact make-up of feedstock 10 and 12 and parameters can be varied to control the quality of the coke product. Experimental testing has proven that the most stringent coke requirement (i.e. for blast furnace use) can be met.

The present technology's primary objective is to produce fuel for the steel industry's iron production blast furnaces. The finished product can also be used in cupolas in the foundry industry as smokeless fuel, or a general carbon fuel source. The technology provides a less expensive, high-performance product with few if any by-product contamination or environmental problems.

The invention may be embodied in other specific forms without departing from the spirit of the central characteristics thereof. The present embodiments therefore to be considered in all respects as illustrative and not restrictive, the core of the invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

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